

Geochemical Characterization of Chromate Contamination in the 100 Area Vadose Zone at the Hanford Site

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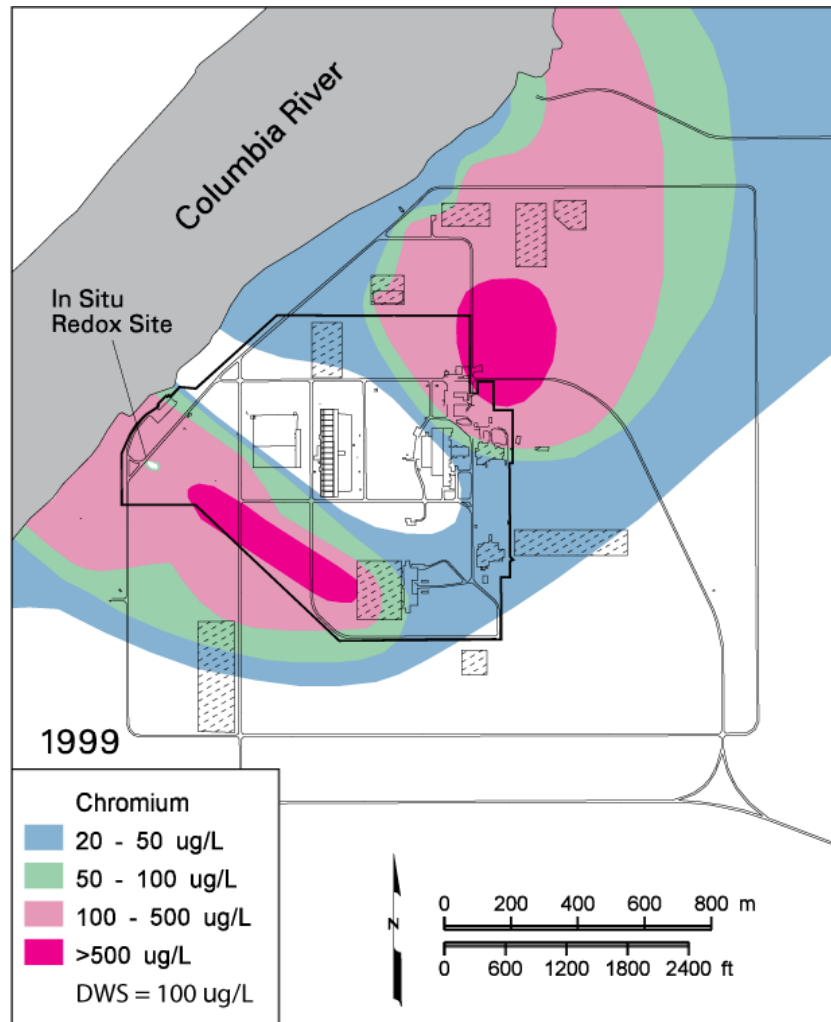
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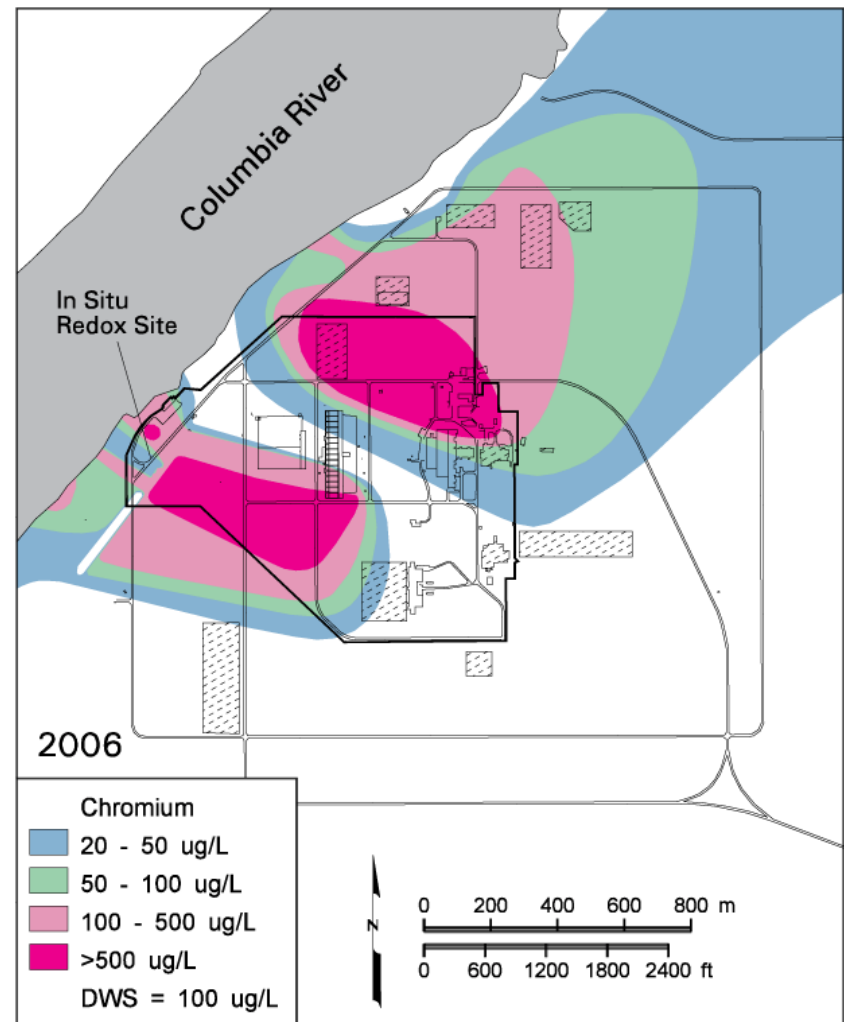
Background

- ▶ Chromate contamination is found throughout the reactor areas at Hanford and is discharging to the Columbia River
 - Maximum concentrations in groundwater >4,000 µg/L
- ▶ Chromate is a particular concern because of the low aquatic water quality criterion.
 - Drinking water standard – 100 µg/L
 - Aquatic water quality criterion – 11 µg/L
 - Surface remediation cleanup target – 2.6 mg/kg
- ▶ Cr(VI) as chromate is known to be poorly sorbed and mobile in groundwater
- ▶ In the vadose zone, at low moisture content, physical and chemical processes that may affect Cr(VI) mobility were not well understood

100-D Area Groundwater Chromate



can_gw104_010a February 15, 2005 4:35 PM



can_gw106_010 February 12, 2007 3:50 PM
wdw07126

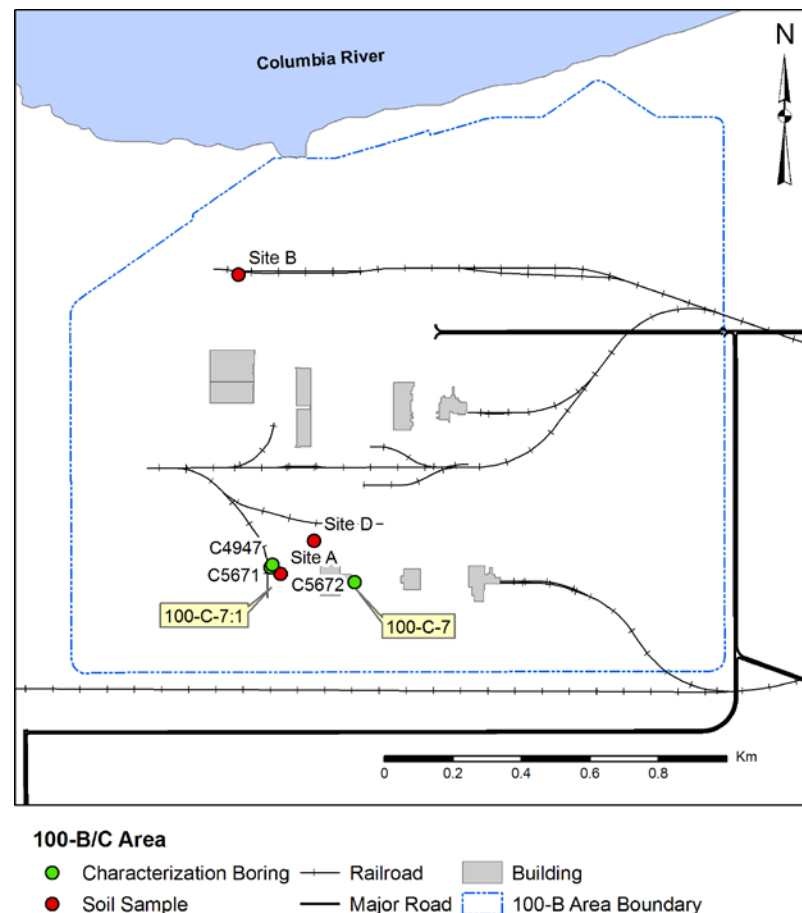
Study Objectives

- ▶ Determine leaching characteristics of Cr(VI) from 100 Area contaminated sediments
- ▶ Elucidate possible Cr(VI) mineral/chemical associations that may be responsible for Cr(VI) retention
 - Macroscopic desorption studies:
 - *column experiments*
 - Micro-scale characterization:
 - *XMP, XRF, XANES, SEM, XPS, XRD*
- ▶ Collect experimental data to develop a conceptual model of Cr(VI) geochemistry in the Hanford vadose zone to provide a basis for testing and selecting potential remedial measures

Sample Collection

► Contaminated samples collected from 100-B area (100-B/C Area)

- Location A – 100-C-7:1 near above ground dichromate and sulfuric acid storage tanks west of water treatment facility
- Location B – Unplanned release, probably from delivery of dry sodium dichromate
- Location D – Shallow samples from recent spill of pipeline liquid
- C5671 – borehole at 100-C-7:1
- C5674 – borehole at 100-C-7, east of water treatment plant



Sample Locations

Location B



Location D



Additional Sample Material

- ▶ 2 uncontaminated sediment samples from 100-D Area
 - PNNL-003 – Black, coarse sand
 - PNNL-004 – Tan sand
- ▶ Pipeline liquid
 - Recovered from pipeline excavated in the 100-D Area
 - ~ 47,000 mg/L chromate

Sample Cr(VI)

Waste Site	Sample Description	Sample	Moisture Content (wt %)	Centrifuge Extracted Cr(VI) (mg/kg)	Water Extractable Cr(VI) (mg/kg)	Alkaline Leach Cr(VI) (mg/kg)
100-C-7:1	~3.7 m bgs. Near-surface concentration prior to excavation was ~1200 mg/kg Cr(VI).	A1	5.95	104.8	99.2	102.6
		A2	11.14	52.6	117.2	350.2
100-B-26	~1.2-1.8 m bgs. Surface stain near railway track. Samples ~40 cm apart.	B1	7.46	387.6	339.7	520.1
		B2	6.88	477.7	465.8	649.4
100-C-7	Location of pipeline rupture during excavation near 183-C-7 Filter Building. Samples ~75 cm apart.	D	6.66	1240.7	810.4	1042.3

Transport Studies

- ▶ Cr(VI) release may be kinetically controlled and rate may be a function of fluid residence time – tested with stop-flow events
- ▶ Magnitude of Cr(VI) rebound during stop-flow and rate of dissipation provide constraints on sequestration degree and mechanisms
- ▶ During late phases of stop-flow, rebound concentrations will likely be limited by solubility of Cr(VI) solid phase if present.

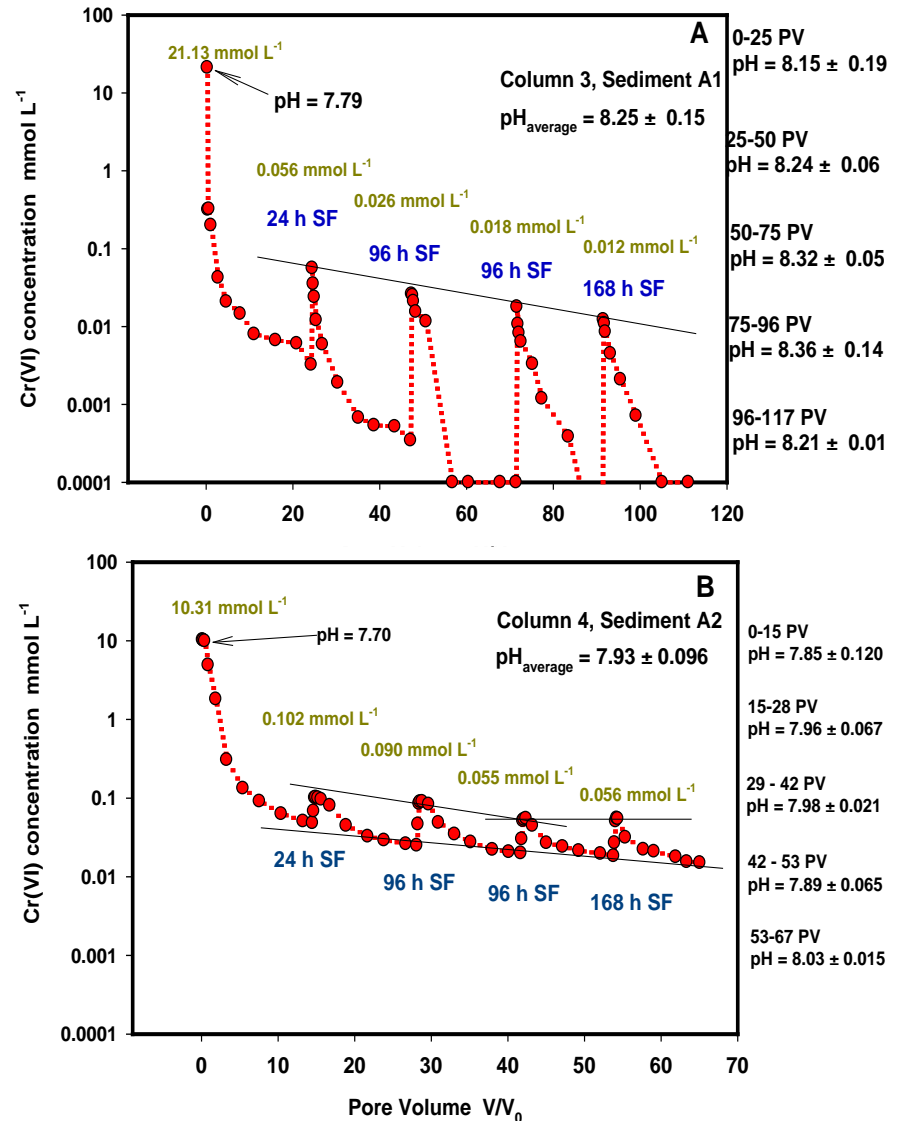
Column Study Methods

- ▶ PVC columns packed in 10 g increments; porous plates placed on each end
- ▶ Synthetic groundwater solution used with bromide as a conservative tracer
- ▶ Effluent collected in a fraction collector; analyzed for Cr(VI), pH, bromide, ICP metals, anions by ion chromatography
- ▶ CXTFIT 1-D equilibrium sorption code used to calculate transport parameters and fit experimental results

Long-Term Column Experiments: Area with Dichromate and Acid Tanks

- ▶ Initial high Cr(VI) declined rapidly with most Cr(VI) released in the first pore volume
- ▶ Long tail indicates the presence of a leaching resistant Cr(VI) pool
- ▶ Initial pH values lower than obtained later
- ▶ pH of location A2 was lower and corresponded to much longer tailing

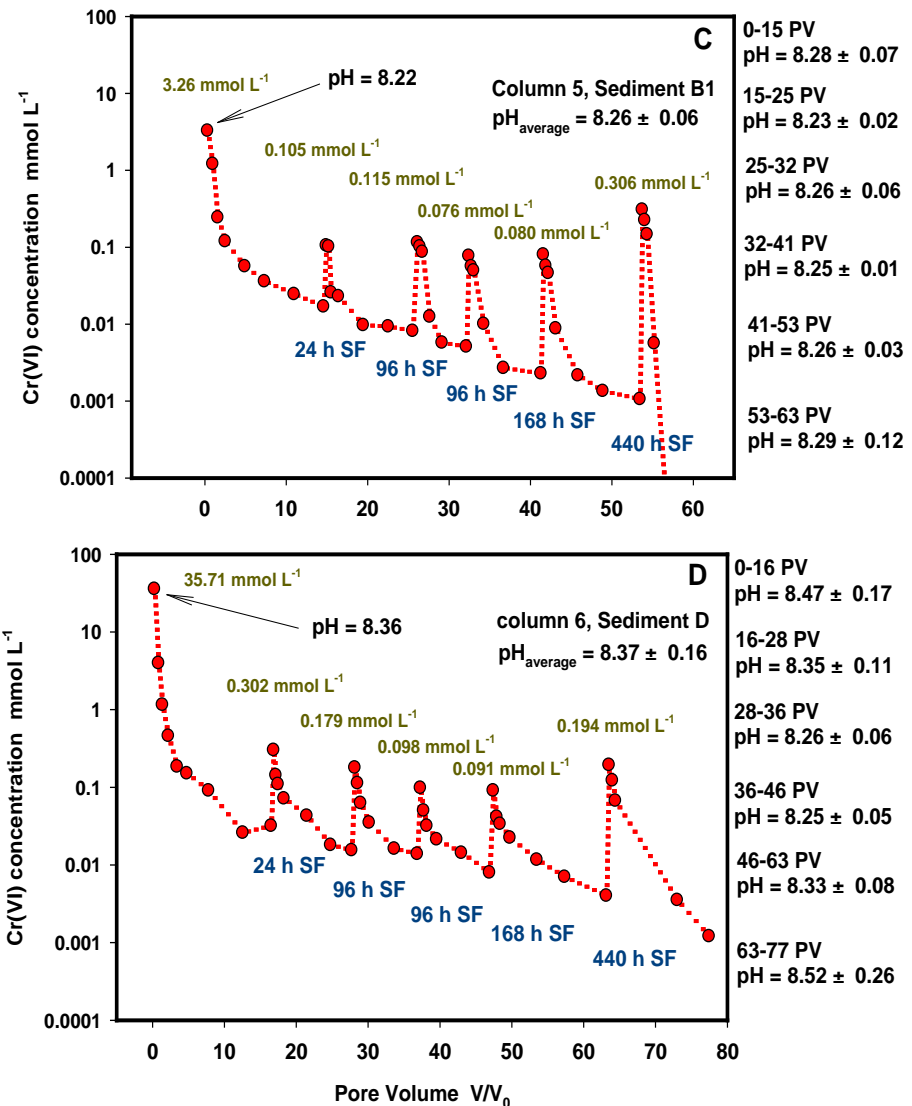
Location A1 Location A2



Long-Term Column Experiments: recent spill vs. aged spill

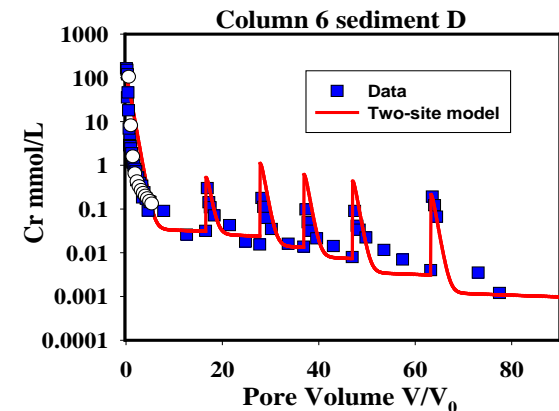
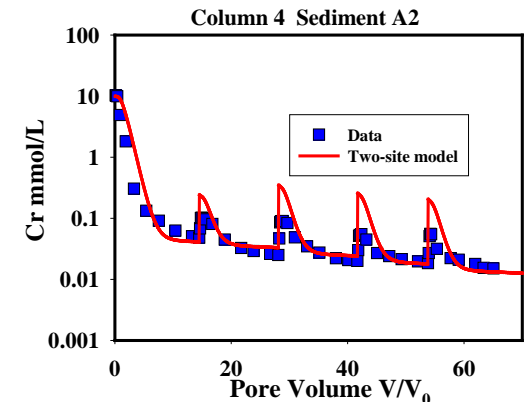
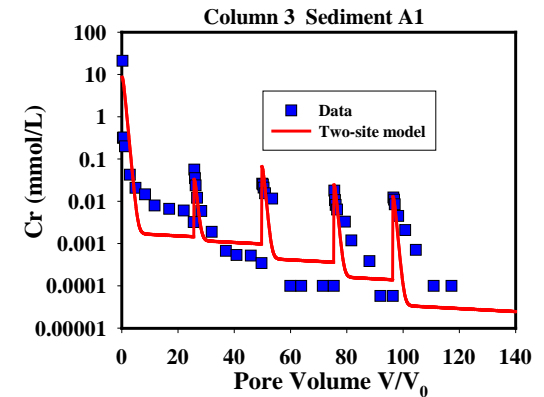
- ▶ Most Cr(VI) released in first pore volume
- ▶ Long tailing shows presence of leaching resistant pool
- ▶ Cr(VI) concentrations remained above drinking water standard (~ 0.0015 mmol/L) for >30 pore volumes
- ▶ Peak concentrations measured in stop-flow events were time dependent. Equilibrium conditions were not attained
- ▶ Peak concentrations between 96 hr stop-flow events decreased due to decreasing mass of Cr(VI) on sediments affects release

Location B, recent spill Location D, aged spill



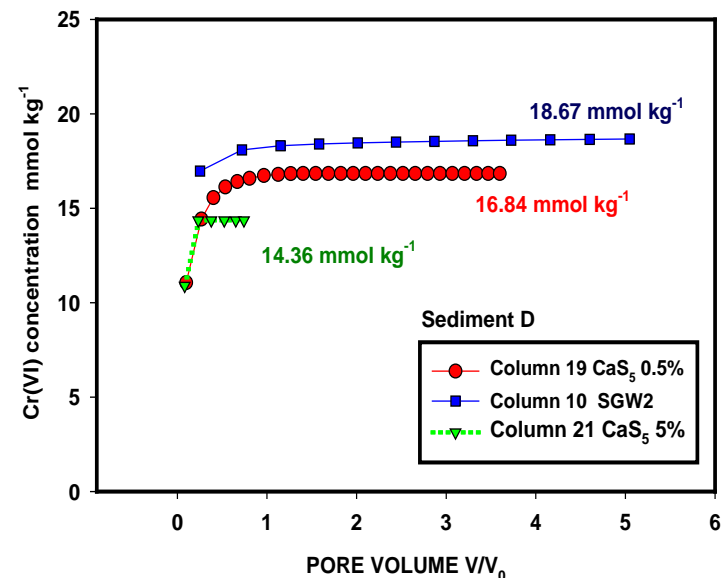
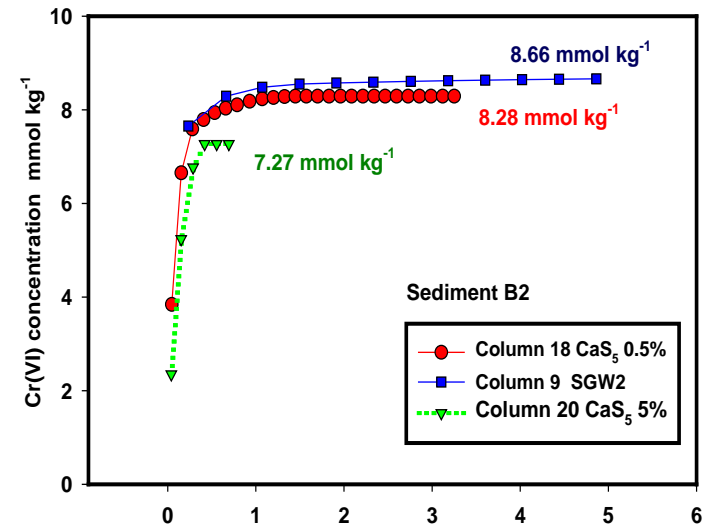
Modeling Results

- ▶ CXTFIT model used to calculate transport parameters base on the bromide breakthrough curves
- ▶ Péclet numbers calculated for experiments were close to 1 indicating mixture of advective and diffusive control on transport
- ▶ Dispersivities < 2 cm were typical for laboratory columns
- ▶ Cr(VI) desorption fit to 2 site model
- ▶ Equilibrium K_D values were close to 0, as expected
- ▶ 95-99% of Cr(VI) in sediments was associated with the equilibrium release fraction
- ▶ Small fraction with time-dependent desorption released with half-lives of 76 – 126 hr.



Contaminated Sediment Reaction with Calcium Polysulfide

- ▶ Sediments packed in columns leached from the bottom up with calcium polysulfide solutions
- ▶ Fluid residence time ~ 2 hr
- ▶ Polysulfide decreased the total amount of Cr(VI) leached but majority of the Cr(VI) was still mobilized in the first pore volume
- ▶ Cr(VI) mobilization at reaction front is an issue that must be considered for remedial schemes using liquid reductants



Transport Experiment Summary

- ▶ The majority of the Cr(VI) mass was transported without significant retardation
- ▶ Experimental data showed at least two Cr(VI) pools (fast and slow releasing) were present in all tested sediments
- ▶ The slow releasing pool was greater in the old spill sediments
- ▶ A two-site model described well the Cr(VI) desorption profiles
- ▶ Mass transfer from poorly accessible domains within sediment matrix was largely responsible for nonequilibrium desorption
- ▶ Barium was not detected in the effluents, indicating that BaCrO_4 (hashemite) or less-soluble $\text{BaCrO}_4 - \text{BaSO}_4$ solid solutions were not controlling Cr(VI) solubility and mobility
- ▶ Injection of strong reductant liquids mobilized the soluble Cr(VI) ahead of the reacting front, limiting the chemical reaction and fixation of the Cr(VI)

Micro-Scale Characterization

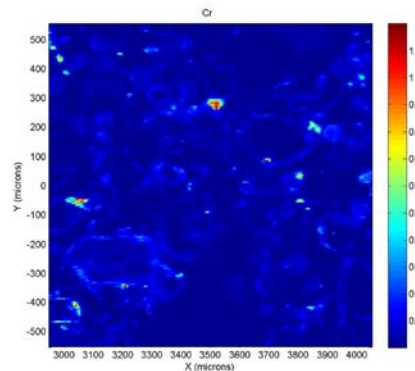
- ▶ Applied a series of microscopic/spectroscopic methods to evaluate the location, valence state, and chemical association of chromium in contaminated sediments
- ▶ **X-ray Microprobe (XMP)**
 - high sensitivity spatial mapping of chemical distributions through X-ray Fluorescence (**XRF**)
 - valence state at selected locations through X-ray Absorption Near Edge Spectroscopy (**XANES**)
- ▶ **Scanning Electron Microscopy (SEM) & Energy Dispersive Spectroscopy (EDS)**
 - used to evaluate mineralogical context of areas of high chromium concentration
- ▶ **X-ray Photoelectron Spectroscopy (XPS)**
 - surface analytical method
 - evaluate chromium valence state

XMP of Contaminated Sediments

- ▶ Thin sections of sediments analyzed
- ▶ Area imaged in 10 μm steps to determine relative concentrations of chromium (and other elements) in sediments
- ▶ Detection limit $\sim 1 \mu\text{g/g}$
- ▶ XANES spectra collected on selected spots
- ▶ Chromium detectable in all samples as grain coatings and discrete grains

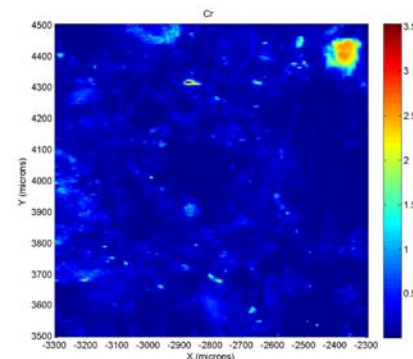
Cr Maps

Location A2
Old Spill



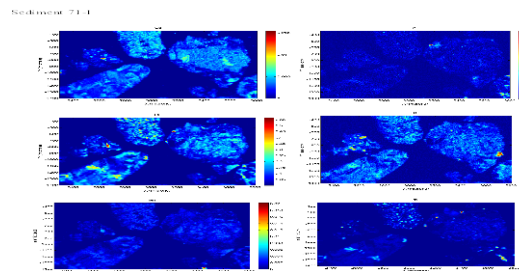
SiteBSample2_Cr .jpg

Location D
Recent Spill



SiteDSample1_Cr .jpg

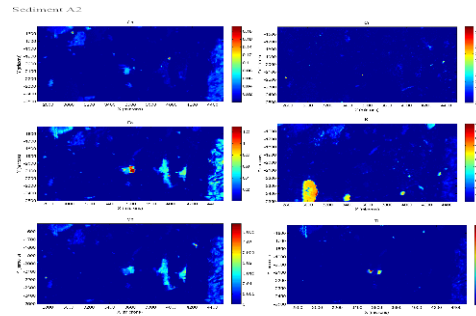
Location 71-1
20 ft bgs



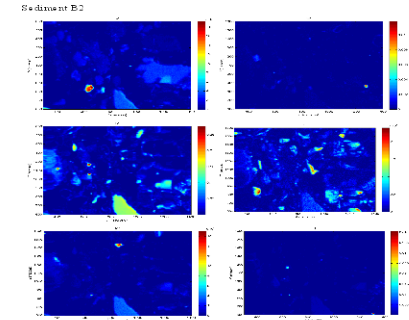
XMP of Leached Sediments

- ▶ Sediments leached with 5 pore volumes of chromium-free synthetic groundwater to remove weakly bound Cr(VI)
- ▶ Leached sediments showed only a weak chromium signal indicating a lack of low mobility chromium phases

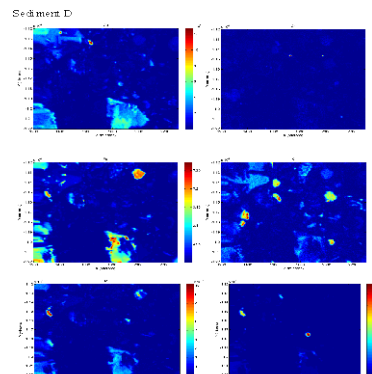
Location A2
Old Spill



Location A2
Old Spill



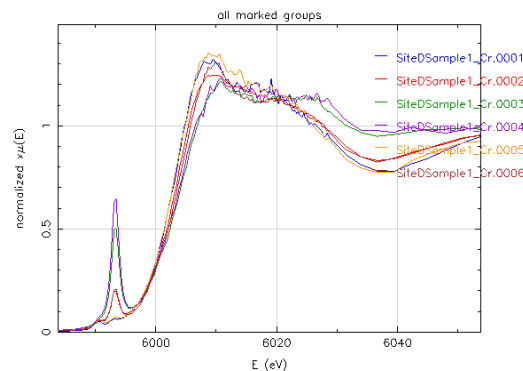
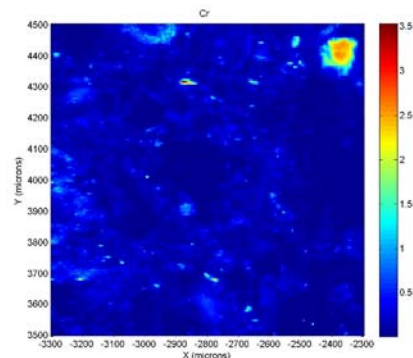
Location D
Recent Spill



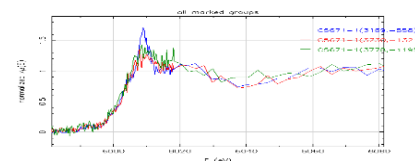
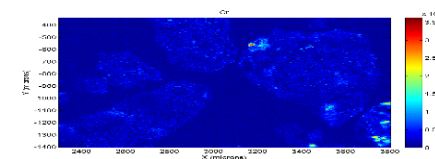
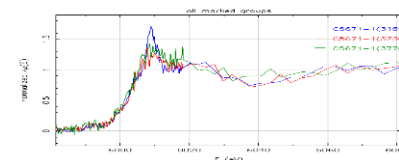
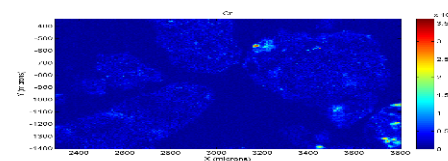
XANES

- ▶ Reduced chromium observed in small concentrated zones within grain coatings
- ▶ Variable Cr(VI):Cr(III) seen at Location A, B, and D
- ▶ Only Cr(III) seen after leaching
- ▶ Sediment 71-1 – only Cr(III) detected

Location D
Recent Spill



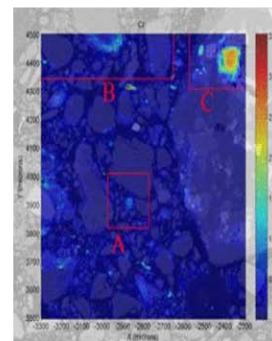
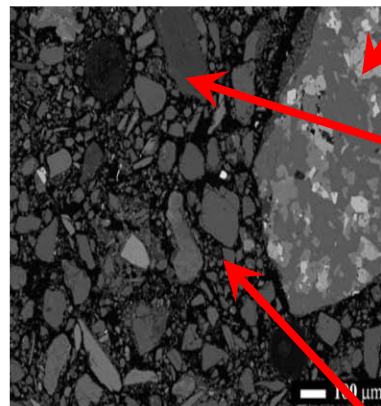
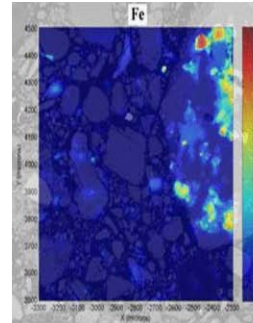
Location 71-1
20 ft bgs



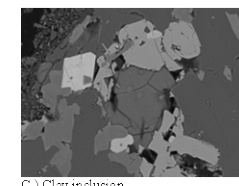
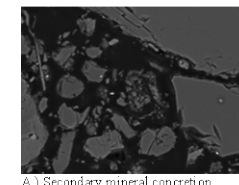
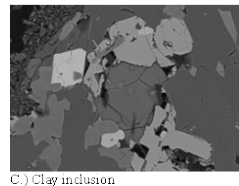
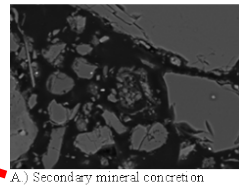
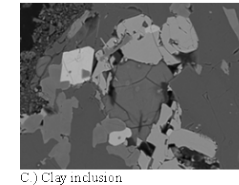
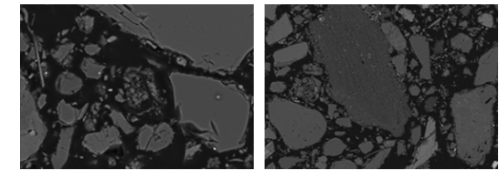
SEM

- ▶ Chromium not detected with EDS
- ▶ XMP maps used to locate area of elevated chromium for SEM examination
- ▶ Elevated chromium associated with secondary mineral phases and clay inclusions
- ▶ May host leaching resistant fraction in pores isolated from advective flow

Fe map



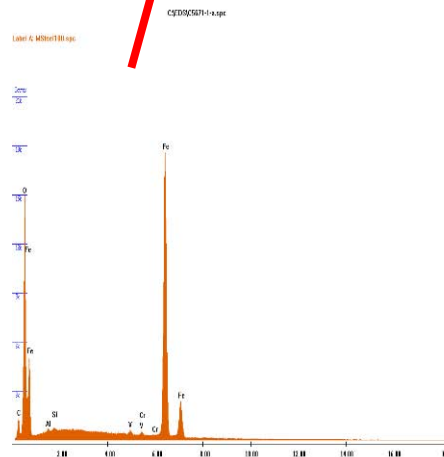
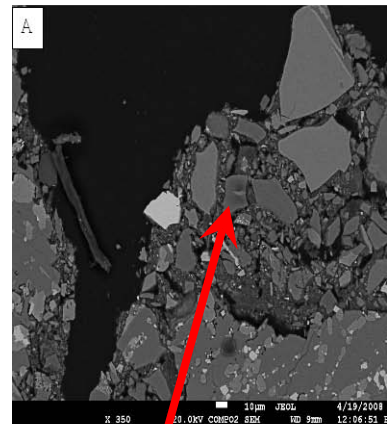
Cr map



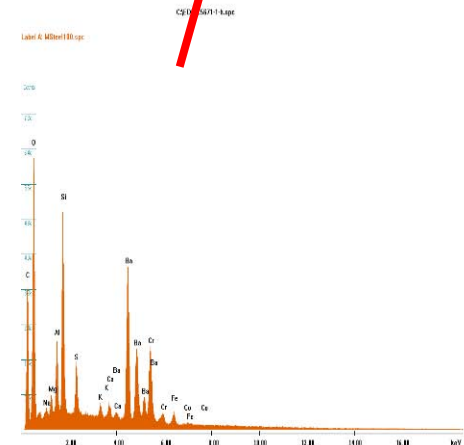
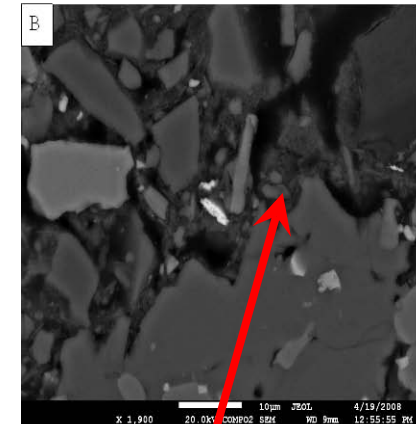
Minor Chromium Phases in 71-1

- ▶ Deeper borehole sample 71-1 showed chromium associated with minor phases
- ▶ One particle associated with iron oxide (likely magnetite)
- ▶ One particle identified as barium chromate

Iron oxide containing chromium

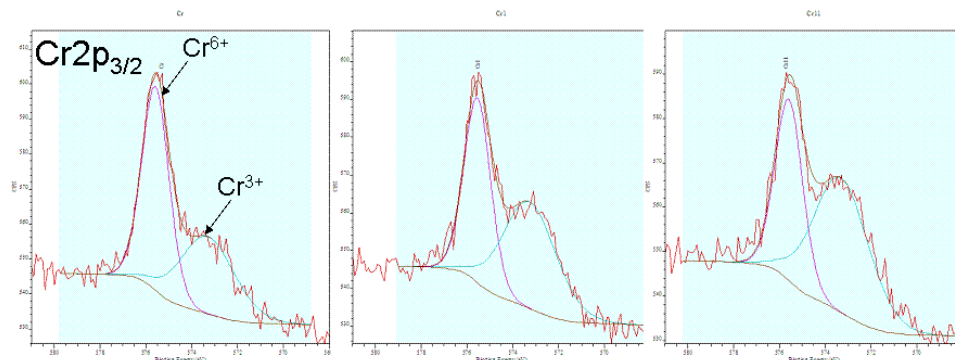


Barium chromate

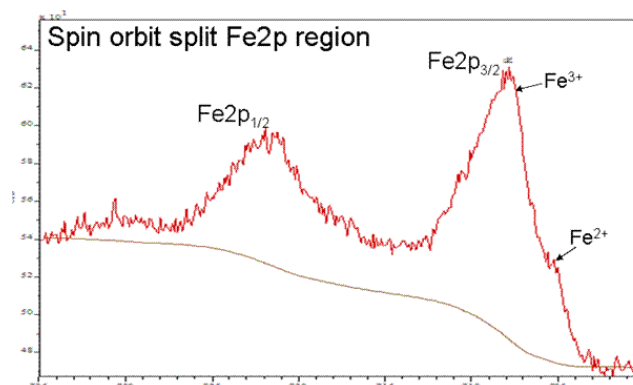
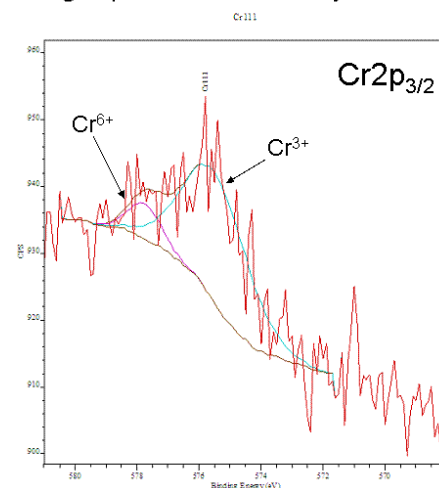


XPS

- ▶ Majority of chromium in unreacted samples present as Cr(VI) with a small fraction of Cr(III) from reduction at surfaces
- ▶ Reduction of Cr(VI) occurred in beam so initial Cr(III):Cr(VI) ratio was estimated from Cr(VI) in unleached samples and Cr(III) in leached samples
- ▶ Surface iron present as mixed Fe(II)/Fe(III) indicating possible mechanism for the limited chromium reduction



Increasing exposure time to X-ray beam →



Summary

- ▶ Contaminant chromium remains dominantly Cr(VI) present as highly mobile chromate that is removed in first pore volume during saturated column leaching experiments
- ▶ A fraction of the Cr(VI) is removed more slowly. The leaching is limited by physical transport/diffusion from restricted pores
- ▶ Minor presence of limited solubility Cr(VI) phases was observed.
- ▶ Some reduction of Cr(VI) to Cr(III) occurs within the sediments but only a fraction of the surface Fe(II) appears accessible for reaction with Cr(VI)

Summary (cont.)

- ▶ Leaching behavior could be adequately described by a 2-site sorption model with one “site” showing essentially no retardation
- ▶ Tailing of Cr(VI) release was greatest in area of co-disposed Cr(VI) and sulfuric acid. The cause of the longer tailing was not apparent in these samples.
- ▶ BaCrO₄ solid was only seen in a sample collected ~20 ft bgs. Minor Cr(VI) reduction observed
 - Question remains as to whether extended contact with sediments during transport to the deep vadose zone (i.e. high sediment to solution ratios/extended reaction progress) will significantly affect the Cr(VI) geochemistry in the deep vadose zone.
- ▶ Cr(VI) in leaching experiments remained above water quality criteria for 10s of pore volumes
 - Impact of slow-release Cr(VI) tailing on groundwater will depend on the recharge rate
- ▶ Liquid reductant mobilized Cr(VI) at solution front so effectiveness for remediation was limited
 - Both physical and chemical processes need to be understood for remedial design